Characterizing Spatial Patterns of Airborne Coarse Particulate ($PM_{10-2.5}$) Mass and Chemical Components in Three Cities: The Multi-Ethnic Study of Atherosclerosis

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Abstract

Background: The long-term health effects of coarse particular matter ($PM_{10-2.5}$) are challenging to assess due to a limited understanding of the spatial variation in $PM_{10-2.5}$ mass and its chemical components.

Objectives: We conducted a spatially intensive field study and developed spatial prediction models for $PM_{10-2.5}$ mass and four selected species (copper, zinc, phosphorus and silicon) in three American cities.

Methods: $PM_{10-2.5}$ snapshot campaigns were conducted in Chicago, Illinois, St. Paul, Minnesota, and Winston-Salem, North Carolina in 2009 for the Multi-Ethnic Study of Atherosclerosis and Coarse Airborne Particulate Matter (MESA Coarse). In each city, samples were collected simultaneously outside the homes of approximately 40 participants during 2-week periods in the winter and/or summer. City-specific and combined prediction models were developed using land use regression (LUR) and universal kriging (UK). Model performance was evaluated by cross-validation (CV).

Results: $PM_{10-2.5}$ mass and species varied within and between cities in a manner that was predictable by geographic covariates. City-specific LUR models generally performed well for total mass (CV R^2, 0.41 to 0.68), copper (CV R^2, 0.51 to 0.86), phosphorus (CV R^2, 0.50 to 0.76), silicon (CV R^2, 0.48 to 0.93) and zinc (CV R^2, 0.36 to 0.73). Models pooled across all cities performed inconsistently at capturing within-city variability. Little difference was observed between the performance of LUR and UK models in predicting concentrations.

Conclusions: Characterization of fine-scale spatial variability of these often heterogeneous pollutants using geographic covariates should reduce exposure misclassification and increase the power of epidemiological studies investigating the long-term health impacts of $PM_{10-2.5}$.

Introduction

Although considerable evidence has linked adverse health with fine particulate matter ($PM_{2.5}$, ≤ 2.5 μm in aerodynamic diameter) (Brook et al. 2010), there has been little epidemiological research examining coarse particulate matter ($PM_{10-2.5}$, 2.5-10 μm in aerodynamic diameter). Toxicological studies have shown that $PM_{10-2.5}$ can induce reactive oxygen species and initiate inflammatory responses *in vivo* and *in vitro* (Becker et al. 2005; Monn and Becker 1999; Pozzi et al. 2003; Schins et al. 2004;Shi et al. 2003;). While this suggests a plausible biological mechanism for long-term health effects, the few studies that have investigated such relationships have generally found weak and non-statistically significant or null associations (USEPA 2006).One possible explanation for differences between the toxicological and epidemiological evidence is that previous epidemiological studies have had a limited ability to characterize spatial variations in $PM_{10-2.5.}$ This can be important since $PM_{10-2.5}$ has relatively short residence times in atmosphere due to high gravitational settling (US EPA 2009) and spatial heterogeneity has been shown to be large (Burton et al. 1996; Chen et al. 2007; Eeftens et al. 2012a; Houthuijs et al. 2001; Wilson and Suh 1997). In addition, there has been limited characterization of spatial differences in $PM_{10-2.5}$ chemical composition which may help to differentiate key sources of $PM_{10-2.5}$ mass (e.g., mineral and roadway dust, sea spray, pollen, and mechanical grinding including vehicular brake and tire wear) (US EPA 2009). Improved understanding of the spatial variation of $PM_{10-2.5}$ mass and chemical components is therefore expected to be critical in quantifying the long-term effects of $PM_{10-2.5}$ exposures.

Since some pollutants, like those from traffic, vary over small spatial scales (i.e., 10-100 meters), there is an increasing emphasis on estimating individual-level exposures (HEI 2010). Regression models with geographic information system (GIS)-derived covariates such as land use, nearby

emission sources, and distance to roadways, termed "land use" regression (LUR) models, are a common approach. Universal kriging (UK) is an extension of this methodology that further incorporates spatial correlations. Although spatial prediction models are commonly employed for $PM_{2.5}$ and oxides of nitrogen (HEI 2010), very few investigations have generated covariate-based spatial prediction models for $PM_{10-2.5}$ and none, to our knowledge, have created a covariate-based, spatial interpolation model for $PM_{10-2.5}$ species.

As part of the Multi-Ethnic Study of Atherosclerosis and Coarse Airborne Particulate Matter (MESA Coarse), we characterized fine-scale spatial differences in $PM_{10-2.5}$ mass and chemical components within three American cities using data from an intensive monitoring campaign. MESA Coarse builds upon the MESA cohort of 6,814 adults from six metropolitan areas (Bild et al. 2002) and the MESA Air Pollution project (MESA Air), which investigates the impacts of $PM_{2.5}$ on the progression of atherosclerosis (Cohen et al., 2009; Kaufman et al., 2012). This paper presents the MESA Coarse field study design and development of spatial prediction models for $PM_{10-2.5}$ mass, copper, zinc, phosphorus, and silicon. These four chemical components were selected because they were shown to be good indicators of brake wear, tire wear, agriculture, and mineral dust, respectively, across all three cities, using positive matrix factorization (Sturtz et al. 2012).

Methods

Sampling Design

$PM_{10-2.5}$ concentrations were measured simultaneously over two 2-week periods in two seasons outside the homes of approximately 40 MESA participants residing in Chicago, Illinois (April 8-22, 2009; and August 20-September 3, 2009), St Paul and Minneapolis, Minnesota (January 17 31, 2009; and May 27-June 10, 2009), and Winston-Salem, North Carolina (February 25-March

11, 2009; and July 6-20, 2009). Homes were selected in a targeted approach that aimed to maximize geographic coverage as well as variability of features believed to be predictive of coarse particles and selected source-specific components. Specifically, we targeted vegetation, distance to major roads, as well as rural, commercial, and industrial land use. While most homes were sampled during one season only, we collected samples during both seasons at approximately one third of homes to assess the stability of concentrations over time. Homes with more unique geographic features were oversampled during the second round to ensure sufficient variability for modeling. Other repeats were selected at random. Institutional Review Boards at each site approved the study and all participants provided written informed consent.

$PM_{10-2.5}$ sampling

Two-week integrated samples were collected using Harvard Personal Environmental Monitors (HPEMs, Thermo Environmental Instruments, Franklin, MA) with Medo VP0125 pumps (Medo, Hanover Park, IL) calibrated to a flow rate of 1.8 liters per minute (lpm), which has been evaluated in ambient field tests against the Harvard Impactor operating at 10 lpm (Lee et al. 2006). To prevent overloading and minimize the number of pumps required, air flow was cycled between paired HPEMs with cut points for PM_{10} and $PM_{2.5}$ every 5 minutes over the two week sampling periods. Programmable timers allowed for the simultaneous collection of samples across all locations in a city.

All Teflon filters were pre-conditioned for $\geq$24-hours at 22.3 ± 1.9°C and 34.7 ± 2.5% relative humidity, prior to weighing by microbalance (Mettler Toledo UMT2, Mettler-Toledo Inc., Highstown, NJ) (Allen et al. 2001). Samples were analyzed for elements by X-ray fluorescence (XRF) spectroscopy by Cooper Environmental Services. Concentrations were estimated by subtracting $PM_{2.5}$ from PM_{10} based on research by Chen and colleagues(Chen et al. 2011).

Many quality control procedures were performed including voiding samples with insufficient durations (<9 days), out-of-range air flows (±20%), damaged filters, extreme concentrations over the two-week sampling period (>5 standard deviations from the mean), and high sulfur levels in the $PM_{10-2.5}$ fraction (>0.2 $\mu g/m^3$) since sulfur should be primarily limited to $PM_{2.5}$. Overall, the precision of duplicate PM_{10}, $PM_{2.5}$, and $PM_{10-2.5}$ samples was 2%, 10% and 18%, respectively. Concentrations were also compared to measurements reported by the Environmental Protection Agency's Air Quality System (AQS) for corresponding time periods during the same year.

Geographic covariates

Table 1 illustrates the covariates derived in ArcGIS 9.3 (ESRI, Redlands, CA) that were considered for our spatial prediction models. They include five major categories: 1) land use such as commercial, industrial, and residential; 2) local transportation including roadways, railways, truck routes, airports, and a traffic dispersion model output; 3) population density; 4) ground cover including impervious surface and vegetation; 5) $PM_{10-2.5}$ emission sources; and 6) positional information (MESA Air, 2011). Briefly, land use data included US Geological Survey satellite-derived raster images from 2000 (Price 2006) and aerial photography from the 1970s and 1980s. Transportation variables were derived from data from TeleAtlas (Lebanon, NH), National Transportation Atlas Database 2009 (Bureau of Transportation Statistics 2009), and the CALINE line source dispersion model (Wilton et al. 2010). $PM_{10-2.5}$ emissions were derived from the National Emission Inventory Database (http://www.epa.gov/air/data/neidb.html), population density was obtained the 2000 US Census Bureau (US Census Bureau 2001), imperviousness was downloaded from the National Land Cover Database 2006 (US Geological Survey 2011), and vegetation was estimated by the Normalized Difference Vegetation Index (NDVI) (Carroll 2008.).

Modeling approach

We utilized LUR and UK to estimate spatial patterns of $PM_{10-2.5}$ mass, copper, zinc, phosphorus, and silicon using approaches previously described by Mercer et al. (Mercer et al. 2011).Our primary models were constructed separately for each city, with season included as a predictor and an effect modifier of other predictors as needed to account for seasonal variation. Pooled models across all cities were also explored in secondary analyses. All stages of this model selection procedure were fit using the glmnet package (Friedman et al. 2010) and R 2.7.2 software (R Development Core Team; http://R-project.org). The resulting prediction models are intended to reflect long-term exposures since preliminary data analyses using AQS monitors in our study regions previously suggested that the average of two-week samples from two seasons was highly correlated with annual average concentrations.

Given the large number of potential predictors, we followed a process of variable screening that began with removal of predictors with insufficient variability (i.e., excluded if 85^{th} percentile equaled the 15^{th} percentile). Then, for variables with varying buffer radii, we selected the 'best' short (50 to 500 m) and long (500 m to 5 km) range buffer based on the highest univariate Pearson correlation coefficient with the exposure being modeled.

Moreover, when multiple predictors were highly correlated with one another ($\rho > 0.85$), we selected the predictor that was most strongly correlated with the exposure, although we preferentially excluded latitude and longitude and selected raster-based land use data (collected in 2000) over older aerial photography-based data (collected in 1970s and 1980s). Next, we applied the least absolute shrinkage and selection operator (LASSO) by changing a tuning parameter to reduce the number of variables down to 15 potential variables or less including both

main effects and interactions by season (and city for the all-city models) (Friedman et al. 2010). Finally, we conducted an exhaustive search to examine all possible combinations of these 15 covariates, restricting to models with 6 or less main effects. We did not consider interactions between predictors other than season or city but did ensure that the main effects were included when an interaction with season or city was included in a model. The final combinations of variables were selected that resulted in the lowest RMSE and the highest R^2under 10-fold cross validation. In this method, the dataset was randomly divided into 10 equal sub-datasets, where model fitting occurred for each selection of 9-tenths of the data while validating on the final tenth. Differences between the true and estimated values of $PM_{10-2.5}$ concentrations for each validation set were then used to calculated RMSE and R^2. This method is intended to avoid over-fitting of the models to the observed data.

Sensitivity analyses were conducted to assess the impacts of: 1) excluding outliers (>3 standard deviations from city-specific means); 2) data sources of land use variables; 3) selecting buffers in a repeated step-wise manner as recommended by Su and colleagues (Su et al. 2009); and 4) natural log-transforming concentrations.

Visualization

Maps were generated by kriging provided by the spatial analysis package in ArcGIS 9.3at a lattice grid over our three cities, with spacing of 0.25 km in urban areas and 1 to 2 km in rural areas.

Results

Measured $PM_{10-2.5}$ mass concentrations

Between January 17 and September 3, 2009, we collected 235 collocated $PM_{2.5}$ and PM_{10} samples. After our quality control procedures were applied, we had 207 (88%) and 195 (83%) valid $PM_{2.5}$ and PM_{10} mass measurements, respectively, resulting in 191 (81%) valid sample pairs from 118 unique locations (56, 25, and 37 in in Chicago, St. Paul and Winston-Salem, respectively, Figure 1). A subset of 34 locations had samples collected during two seasons: 4, 17, and 13 in Chicago, St. Paul and Winston-Salem, respectively.

Table 2 summarizes $PM_{10-2.5}$ mass and species concentrations by city and season (see Supplemental Material, Table S1 for detailed descriptive statistics). Average $PM_{10-2.5}$ concentrations (standard deviation) across seasons were 5.7 ± 2.0, 5.3 ± 3.3 and 3.6 ± 1.4 $\mu g/m^3$ in Chicago, St. Paul and Winston-Salem, respectively. A strong seasonal difference was seen in St. Paul (3.3 ± 2.2 and 6.7 ± 3.3 $\mu g/m^3$ in winter and summer, respectively) but not the other two cities (Chicago: 5.5 ± 2.0 and 5.9 ± 2.1 $\mu g/m^3$ in winter/early spring and summer, respectively; and Winston-Salem: 3.5 ± 1.2 and 3.8 ± 1.6 $\mu g/m^3$ in winter and summer, respectively).

Silicon had the largest observed species concentrations, with levels 12 to 260 times larger than the three other species (Table 2). Especially high concentrations of silicon were observed in St Paul during the summer (720 $\pm$ 188 ng/m^3) whereas the other two cities had lower levels that peaked in the winter. Phosphorus concentrations in all three cities were highest in the summer, with an approximate doubling of concentrations as compared to the winter in St Paul and Winston-Salem. In contrast to the other pollutants that had similar concentration ranges across cities, copper and zinc concentrations differed by location, with the highest levels of both observed in Chicago, and the lowest levels in Winston-Salem. Zinc was the most variable species

in each of the three cities during both the winter (coefficient of variation defined as standard deviation over mean: 0.75 to 0.81) and summer (coefficient of variation: 0.69 to 1.27).

Spatial modeling results

Data reduction procedures reduced the overall number of potential predictors from 802 to between 64 to 94, and the LASSO procedure further reduced the number of candidate predictors to approximately 15 for each city and species. Final models included 7-8 main effect predictors and up to 4 interactions (with season in the city-specific models, and with season or city in the all-city models) (see Supplemental Material, Tables S2-S6 for lists of the predictors included in each final model according to city and exposure.).

Overall our models fit the data well (Figure 2), explaining between 36 and 93% of the variability in $PM_{10-2.5}$ mass and species concentrations under cross-validation (Table 3). For all cities, LUR always had comparable predictive performance as UK. Our LUR models performed generally better in Chicago and St. Paul compared to Winston-Salem, and had the most consistent predictive ability for silicon in models including data for all cities. The other models pooled across all cities demonstrated inconsistent performance at capturing within-city variability with the best within-city CV R^2 ranging from 0.54 to 0.66 as compared to 0.0 to 0.34 for cities with the worst predictions. Again, UK models pooled across all cities generally had similar or lower model performance than their corresponding LUR models.

Figure 1 shows the spatial patterns and distributions of predicted concentrations by city. $PM_{10-2.5}$ mass, silicon, and phosphorus had similar prediction ranges across all cities, whereas copper and zinc showed much higher predictions in Chicago and St Paul than Winston-Salem. The highest $PM_{10-2.5}$ mass predictions were for the urban centers of Chicago and St Paul but in

Winston-Salem higher levels were predicted outside of the urban core. Across all three cities, copper and zinc exhibited higher concentrations in urban areas, with elevations of copper focused in areas of high intensity land use and along major roadways. Zinc was more evenly distributed throughout the Chicago and St Paul but was patterned with roadways in Winston-Salem. Silicon was highest in St Paul and most variable in Chicago where high concentrations were focused along an industrial corridor to the west of the city and lowest concentrations were found in the outlying areas. Phosphorus was similarly patterned in Chicago but less concentrated downtown. Predictions were highly variable for phosphorus in St Paul but consistently high in Winston-Salem, with higher predictions in the outlying areas.

Supplemental Material, Tables S2-S6 show the estimated coefficients of the LUR models by city and pooled across cities. In general, $PM_{10-2.5}$ mass, copper and zinc concentrations were associated with traffic-related features across the three cities (e.g., land use, distance to roads, sum of road length and sum of truck route lengths). Models for phosphorus and silicon concentrations consistently included vegetation features as predictors in St. Paul and Winston-Salem, but also included water features in Chicago. Vegetation appeared predictive across all mass and species models in Winston-Salem. Medium or high intensity of urban land use was predictive among all models for total mass and sum of road length was consistently included in all pooled models as were season and city.

Sensitivity analyses indicated that two extreme measurements from St Paul were influential with weaker predictive performance without the outliers (CV R^2 0.51 as compared to 0.65). Slightly improved model performance was found using land use from both the raster data and aerial photography as compared to either alone (Supplemental Material, Table S7). Models based on the natural log of $PM_{10-2.5}$ levels and the iterative covariate selection approach proposed by Su

and colleagues (Su et al. 2009) showed generally poorer prediction performance as denoted by lower CV R^2 and higher RMSE than those presented here (data not shown).

Discussion

This study conducted spatially intensive $PM_{10-2.5}$ sampling and developed two types of spatial prediction models (LUR and UK) for $PM_{10-2.5}$ mass and chemical components (copper, phosphorus, silicon and zinc) for use in the MESA Coarse epidemiology study. To our knowledge, this is one of the first studies to develop fine-scale spatial prediction models for $PM_{10-2.5}$ mass and chemical components, which can serve as tracers for different sources of pollution. We demonstrated that geographic covariates can explain within-city variations in concentrations (mean CV R^2: 0.61) though the predictive power varies across cities and species (range of CV R^2: 0.36 to 0.93). By capturing fine-scale spatial variability of these often heterogeneous pollutants, this work is expected to substantially reduce measurement error and improve our ability to investigate the long-term health impacts of $PM_{10-2.5}$ over traditional approaches that rely on a limited number of central monitoring stations.

Across all models, there was some similarity in the spatial features predictive of concentrations, including high and medium intensity land use and indicators of traffic and vegetation, yet there was limited commonality in the key predictors. For example, variables related to traffic, high/medium development and residential areas were consistently selected in final models in Chicago, while indicators of vegetation were more consistently included in final models in Winston-Salem. This is consistent with the fact that Chicago is a more industrialized city with higher concentrations of copper and zinc than Winston-Salem, which is a smaller city. Similarly, water features appeared to be a stronger predictor of $PM_{10-2.5}$ particles in St Paul than the other cities as this is a prominent feature of this region. Season modified the influence of certain

predictors, as would be expected given the presence of snow cover during winter periods in St Paul and Chicago and changes in vegetation across all areas. Although other characteristics of seasonality may influence $PM_{10-2.5}$ concentrations, we did not have fine-scale spatial meteorology data to explicitly explore these associations. An analysis of wind speed and direction, however, failed to show a strong prevailing wind direction during our sampling periods suggesting that wind is likely not a strong predictor or modifier of concentrations. In addition, we did not identify important differences between our sampling periods and other typical weeks suggesting that our results should be representative of other time periods. Related to these area-specific differences, we were unable to identify robust predictions of within-city variability based on the same models for all cities (Supplemental Material, Tables S2-S6). Though some of our pooled models showed good performance in more than one city, no model worked well in all locations. Thus, while it is possible that these models may be generalized to other cities with similar characteristics, further validation is warranted before broad application.

Predictive performance of our models was consistent with the one study from Europe and generally better than the few $PM_{10-2.5}$ models in the United States. Using 20 to 40 monitoring stations in each of 20 European areas, similar CV R^2 were reported as in our study (Eeftens CV R^2: 0.03 to 0.73; Our MESA Coarse study CV R^2: 0.41 to 0.68.) (Eeftens et al. 2012b). In a recent study from Ohio, Mukerjee et al. (2012) reported a R^2 of 0.78 for their LUR model. As this was not derived from cross-validation in which some data is withheld from the model building step for validation, however, the predictive power would be inflated due to issues of overfitting. Also in the US, Yanosky and colleagues showed CV R^2 values for $PM_{10-2.5}$ were 0.39 and 0.33 after and before 1999 for cities across the Northeastern and Midwestern United States, respectively. (Yanosky et al. 2009) Their lower predictive performance can be likely be

explained by their use of regulatory monitors, which are more sparse and reflect less variation in geographical predictors than the intensive campaigns of this, the European, and Ohio studies. Predicting $PM_{10-2.5}$ indirectly by modeling $PM_{2.5}$ and PM_{10} separately may also have influenced their models. Independent of the source of data, we generally found similar predictors to past work including proximity to roadways, land use, and vegetation. Also like our study, Eeftens et al. (2012b) indicates that key covariates differed by city.

UK performed similarly to LUR for all cities suggesting limited spatial correlation of $PM_{10-2.5}$ after control for geographic covariates. An alternative explanation is that our relatively small sample size (N~30 to 40 locations in each city) may have limited the ability of our models to characterize fine-scale spatial structure of $PM_{10-2.5}$. Our models should have captured at least some of the small scale correlation structure, if it substantially influenced predictions, given that distances between some of the sampled residences were small (minimum distances of 8, 64, and 174 meters in Chicago, St. Paul, and Winston-Salem, respectively).

Measured $PM_{10-2.5}$ levels were generally lower than those reported in other major and small cities of the U.S, possibly because our study samples were exclusively collected at residual locations where there may be fewer sources of $PM_{10-2.5}$. The average levels of $PM_{10-2.5}$ measured at study locations in both Chicago and St. Paul (5-6 $\mu g/m^3$) were comparable to those reported in residential neighborhoods in Detroit (6-7 $\mu g/m^3$) (Thornburg et al. 2009), but much lower than reported for a variety of sites in Los Angles (5-14 $\mu g/m^3$) (Pakbin et al. 2010), Philadelphia (5-9 $\mu g/m^3$) (Burton et al. 1996), Denver (9-6 $\mu g/m^3$) (Clements et al. 2012) , Research Triangle Park (1-13 $\mu g/m^3$) (Chen et al. 2007),and Central and Eastern European countries (12-40 and 6-24 $\mu g/m^3$) (Houthuijs et al. 2001; Eeftens et al. 2012a). While our means were lower, study

locations with the highest measured concentrations (12μg/m^3 in Chicago and 17 μg/m^3 in St Paul) were in line with concentrations reported by these other studies.

Spatial variability also was lower than expected, which may also be due to sampling from residential locations only. Average $PM_{10-2.5}$ concentrations were, however, generally comparable to those estimated by concurrent PM_{10} and $PM_{2.5}$ AQS samples during the same two-week sampling periods. For example, the two-week averages of 4 available Chicago AQS sites were 4.5 ± 5.3 and 6.1 ± 2.1 μg/m^3 when we reported 5.5 ± 2.0 μg/m^3 and 5.9 ± 2.1 μg/m^3 in matched time periods. In Winston-Salem, one available AQS site had one two-week average of 3.7 ± 1.5 μg/m^3 when we observed 3.8 ± 1.6 μg/m^3 and 2.4 ± 0.2 μg/m^3 when we observed 3.5 ± 1.2 μg/m^3. In St. Paul, two available AQS sites had two-week mean levels of 6.6 ± 4.7 and 8.6 ± 4.6 μg/m^3 when our reported concentrations were 3.3 ± 2.2 and 6.7 ± 3.3 μg/ m^3, respectively.

This study has a few important strengths. First, we collected spatially-intensive samples of $PM_{10-2.5}$ using the same sampling protocol in three US cities. Using a snapshot style campaign, we were able to predict $PM_{10-2.5}$ mass at unmeasured locations based on geographic characteristics of that precise location. This represents a substantial improvement for predicting long-term concentrations at unmeasured locations compared to assigning the concentration of the nearest monitor or simple interpolation methods that do not consider the characteristics of a location other than latitude and longitude (e.g., inverse distance weighted method and ordinary kriging). By including chemical speciation of these particles, we are also the first to our knowledge to predict the spatial distribution of $PM_{10-2.5}$components. This is important since components can be used as indicators of different source types in the related health study. This study has a few limitations. First, we used repeated two-week samples over one year to assess long-term exposures to $PM_{10-2.5}$. While not an annual average, our sampling duration should be

sufficiently long to mitigate transient perturbations such as transient meteorological fluctuations and reflect average conditions. Comparisons with available data from AQS monitors suggest that average $PM_{10-2.5}$ mass during our two-week sampling periods were highly correlated with, and within 15% of, the annual averages at the AQS stations. However, we cannot confirm our estimates for $PM_{10-2.5}$ components, as measured values are not available for comparison. Additionally, our models were derived based on data collected during a single year, and thus may not be accurate for other time periods if spatial patterns vary over time. Spatial stability has been recently demonstrated for traffic-related gases in Vancouver over 7 years (Wang et al. 2013) but is not guaranteed in other locations or for other pollutants. Other limitations pertain to our sampling locations. Although we attempted to capture different land uses, samples were collected at the homes of MESA participants thus our models may be more appropriate for predicting concentrations in residential areas than in industrial or commercial areas.. In addition, our models may not have captured very small scale spatial correlations, as only a few of the sampling locations were located within 100 meters of one another. Finally, while each component targeted for this analysis was intended to be common predictors of brake wear, tire wear, agriculture, and mineral dust across all cities, some caution is warranted in the strict interpretation of these indicator species since our tracers were not always unique to a single source (Sturtz et al. 2014). Research is ongoing to explore the spatial patterning of individual source contributions in further detail.

Conclusions

In summary, we demonstrated that a spatially intensive monitoring campaign was useful in predicting fine-scale spatial variability of $PM_{10-2.5}$ mass and chemical component concentrations within and across three US cities. This research and the resulting prediction models represent a

substantial improvement for epidemiology over studies of $PM_{10-2.5}$ that have previously assigned pollutant concentrations from a central site to an entire city. Some differences in predictive performance by city and species, however, implies that caution should be taken in epidemiology studies when drawing inferences about the comparative health impacts of pollutants estimated by these types of models. As such, investigators should be mindful that any observed differences in apparent toxicity may also be, at least partly, attributable to differential accuracy in estimating concentrations.

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Table 1. Variables considered for spatial prediction models for $PM_{10-2.5}$ mass and chemical component concentrations.

Variables	Units	Buffer radii
Land use: Satellite based		
Open water; Perennial ice or snow; Developed open space; Developed low intensity; Developed medium intensity; Developed high intensity; Bare rock/sand/barren/mine; Tree; Shrub land; Grasslands/herbaceous vegetation; Pasture/hay; Cultivated crops; and Woody wetlands.	%	50, 100, 150, 300, 400, 500, 750, 1000, 1500, 3000, 5000m
Land use: Aerial photography based		
Residential; Commercial and services; Industrial, Transportation, communications, and utilities; Other urban or built-up land; Mixed urban or built-up land; Strip mines, quarries, and gravel pits; Industrial and commercial complexes; and Transitional areas.	%	50, 100, 150m
Transportation		
Distance to the nearest A1/A2/A3 road	m	NA
Length of A1/A2/A3 roads in buffers	m	50, 100, 150, 300, 400, 500, 750, 1000, 1500, 3000, 5000m
Distance to the nearest truck route/railroad/rail yard/airport/large port	m	
Length of truck routes in buffers	m	100, 150, 300, 400,500, 750, 1000, 1500, 3000, 5000. 10000, 15000m
CALINE long-term average[a]	NA	1.5km, 3km, 4.5km, 6km, 7.5km, 9km
Population density		
Population density	Person km^{-2}	3km, 5km, 10km, 15km
Emissions		
Sum $PM_{10-2.5}$ emissions	tons $year^{-1}$	<3 km, 3-15 km, 3-30 km
Physical geographic information		
Latitude and longitude (X,Y)	m	NA
Distance to main and local city hall	m	NA
Imperviousness and NDVI[b]		
Imperviousness	%	50, 100, 150, 300, 400, 500, 750, 1000, 3000, 5000 m
NDVI in the 25 and 75 percentiles	NA	250, 500, 1000, 5000 m

[a]CALINE long term average concentrations of a traffic-generated inert gaseous pollutant were generated from a line source dispersion model (CALINE3QHCR). [b]Normalized Difference Vegetation Index.

Table 2. Summary of statistics (mean ± SD) for $PM_{10-2.5}$ mass ($\mu g/m^3$) and chemical component (ng/m^3) concentrations in each sampling city by season.

City and Season [a]	N	Total mass	Cu	P	Si	Zn
Chicago, IL						
Winter	33[b]	5.54 ± 1.98	7.83 ± 3.32	13.64 ± 6.00	428.24 ± 105.37	23.74 ± 18.36
Summer	31	5.94 ± 2.09	7.10 ± 4.37	17.87 ± 3.87	306.84 ± 157.92	25.87 ± 22.85
Pooled	64[c]	5.73 ± 2.03	7.47 ± 3.86	15.72 ± 5.46	368.51 ± 146.16	24.79 ± 20.55
St. Paul, MN						
Winter	25	3.34 ± 2.22	4.01 ± 1.23	8.20 ± 4.68	266.04 ± 41.13	5.23 ± 3.42
Summer	34	6.66 ± 3.33	2.77 ± 1.69	18.67 ± 5.44	719.31 ± 188.23	5.55 ± 7.03
Pooled	59	5.25 ± 3.33	3.29 ± 1.63	14.23 ± 7.29	527.25 ± 268.13	5.42 ± 5.74
Winston-Salem, NC						
Winter	35	3.46 ± 1.21	2.57 ± 1.23	12.83 ± 3.70	410.63 ± 85.93	3.31 ± 2.67
Summer	28	3.83 ± 1.64	2.57 ± 1.46	25.90 ± 5.71	345.90 ± 109.79	2.76 ± 1.95
Pooled	63	3.63 ± 1.42	2.57 ± 1.33	18.64 ± 8.04	381.86 ± 101.74	3.07 ± 2.37

[a]All sampling was conducted in 2009. Chicago: winter April 8–22, summer August 20–September 3; St. Paul: winter January 17–31, summer May 27–June 10; Winston-Salem: winter February 25–March 11, summer July 6–20. [b]32 for the four species. [c]63 for the four species.

Table 3. Model performance (cross validated R^2 and RMSE) for $PM_{10-2.5}$ mass ($\mu g/m^3$) and species concentrations (ng/m^3) using land use regression (LUR) and universal kriging (UK).

Model	CV Measure	Total Mass	Cu	P	Si	Zn
Land Use Regression[a]						
Chicago, IL	R^2	0.68	0.65	0.50	0.68	0.73
Chicago, IL	RMSE	1.16	2.29	3.88	82.10	10.63
St Paul, MN	R^2	0.51	0.86	0.68	0.93	0.40
St Paul, MN	RMSE	2.33	0.61	4.14	72.60	4.44
Winston Salem, NC	R^2	0.41	0.51	0.76	0.48	0.36
Winston Salem, NC	RMSE	1.09	0.93	3.95	73.10	1.89
All cities[b]	R^2	0.52, 0.54, 0.10	0.65, 0.49, 0.09	0.34, 0.59, 0.66	0.24, 0.64, 0	0.61, 0, 0
All cities[b]	RMSE	1.39, 2.24, 1.33	2.26, 1.06, 1.25	4.39, 4.63, 4.66	126.36, 160.06, 119.10	12.72, 6.10, 3.58
Universal Kriging						
Chicago, IL	R^2	0.68	0.64	0.50	0.68	0.73
Chicago, IL	RMSE	1.14	2.32	3.88	82.60	10.60
St Paul, MN	R^2	0.51	0.86	0.68	0.91	0.38
St Paul, MN	RMSE	2.32	0.61	4.14	82.80	4.52
Winston Salem, NC	R^2	0.41	0.51	0.76	0.47	0.36
Winston Salem, NC	RMSE	1.09	0.93	3.95	74.10	1.89
All cities	R^2	0.51, 0.52, 0.11	0.20, 0.20, 0	0.15, 0.38, 0.65	0.22, 0.64, 0	0, 0, 0
All cities	RMSE	1.42, 2.29, 1.33	3.42, 1.34, 2.10	5.00, 5.67, 4.78	128.41, 159.27, 132.77	22.01, 7.66, 10.58

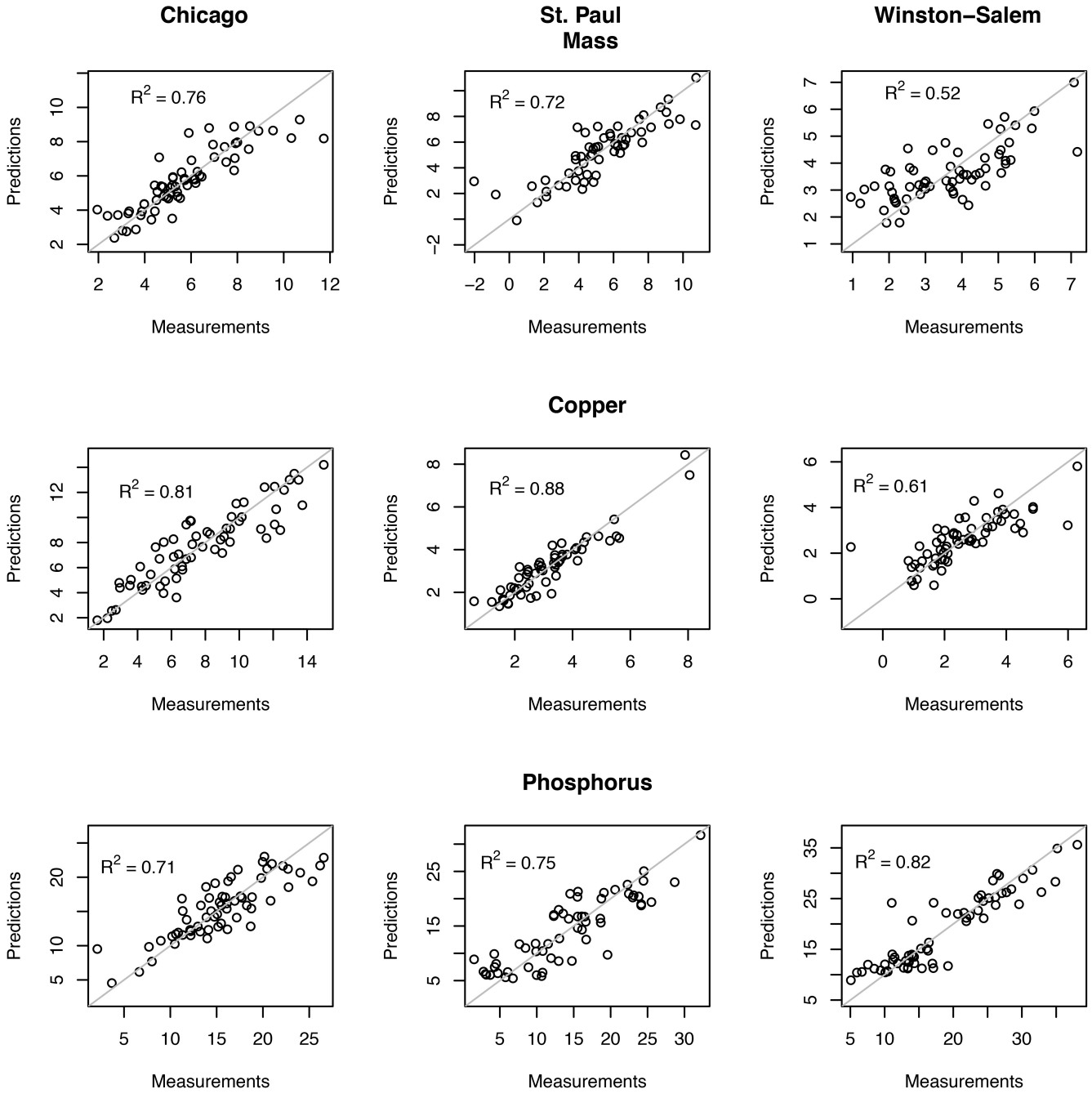
[a]The predictors included in each model are listed in Supplemental Material, Tables S2-S6. [b]For pooled models across all cities we present the R^2 for the explanatory power of each city as calculated by the formula (1 – sum of squared differences between observations and predictions / sum of squared differences between observations and city-specific means). We report any R^2 with values less than 0 as 0. We report the RMSE for each city and calculated RMSE as the square root of the average of squared differences between observations and predictions. The respective R^2 and RMSE values for each city are presented in the following order: Chicago, St. Paul, Winston-Salem.

Figure legends

Figure 1. MESA Coarse measured vs. predicted concentrations for $PM_{10-2.5}$ mass and chemical components in three US cities.

Figure 2. Scatter plots between observations and the predictions from the "best" land use regression models by city and species (R^2 = square of correlations between measurements and predictions).

Figure 1.


Chicago
R2 = 0.76
St. Paul
Mass
R2 = 0.72
Winston−Salem
R2 = 0.52
Copper
R2 = 0.81
R2 = 0.88
R2 = 0.61
Phosphorus
R2 = 0.71
R2 = 0.75
R2 = 0.82
Predictions
Measurements

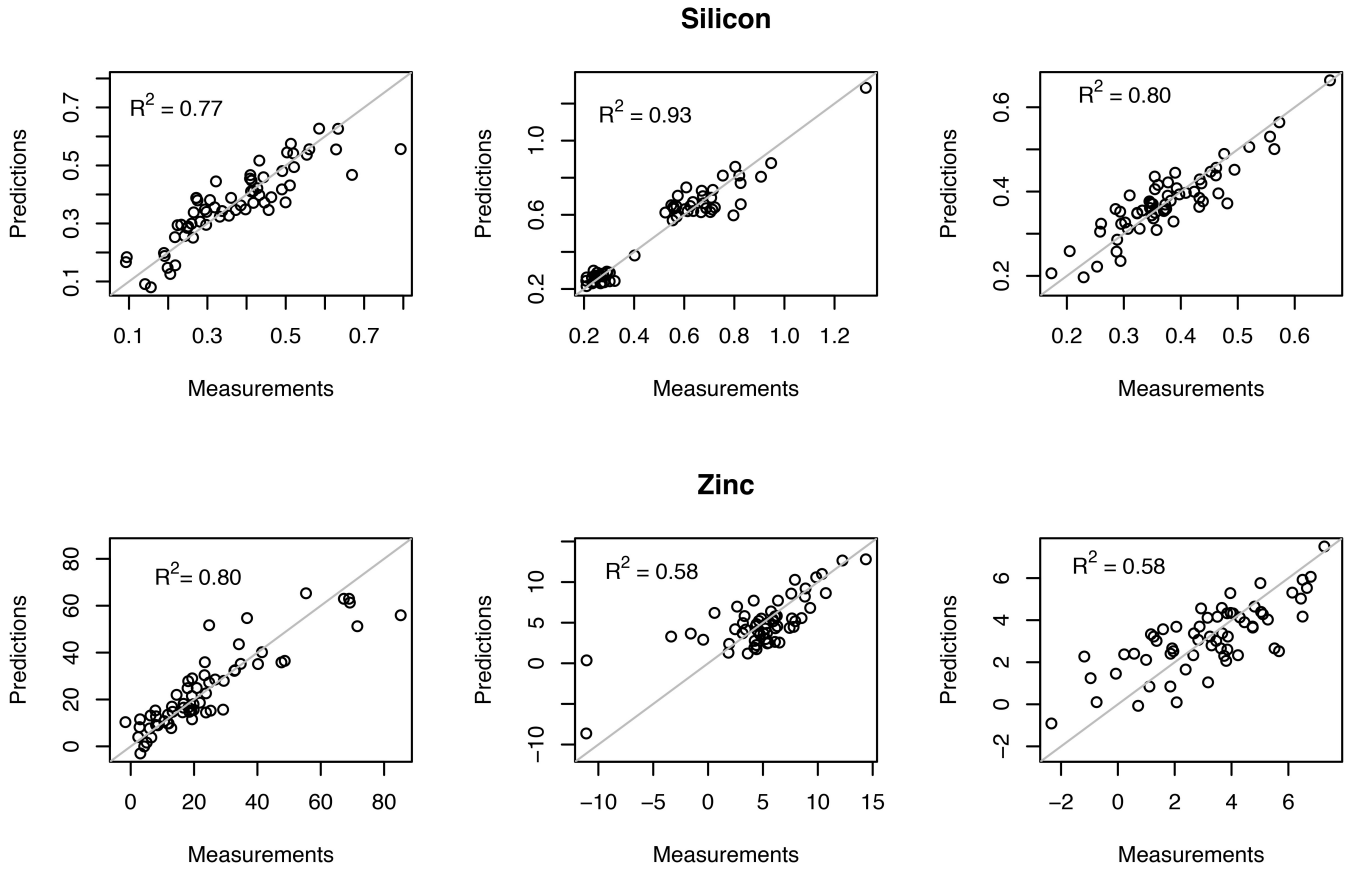
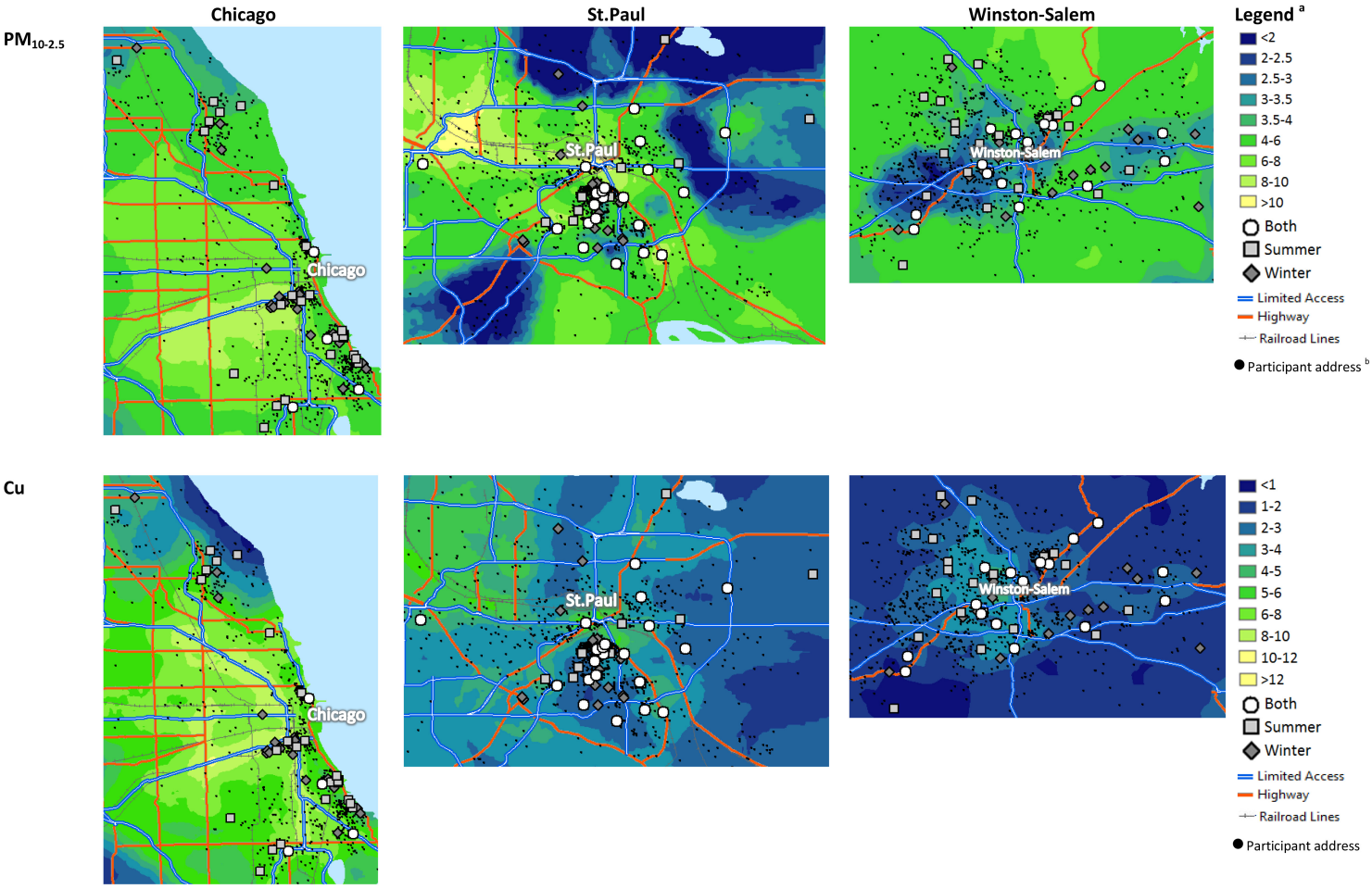
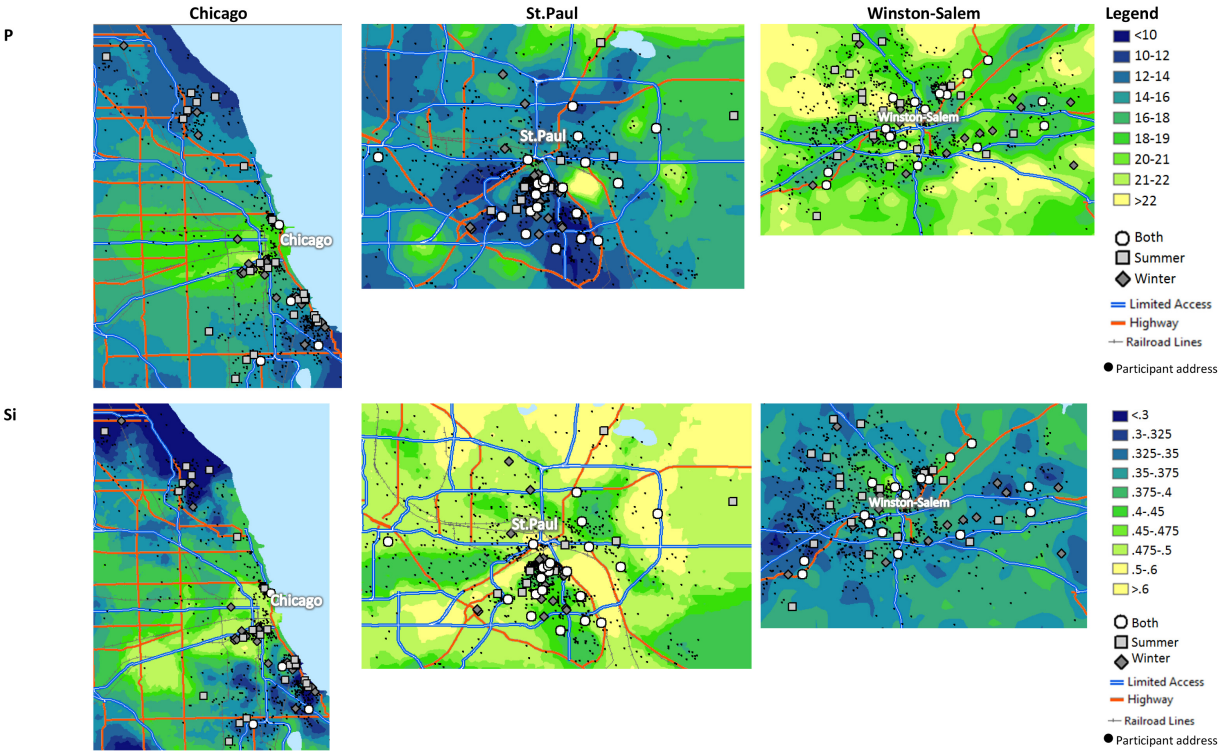
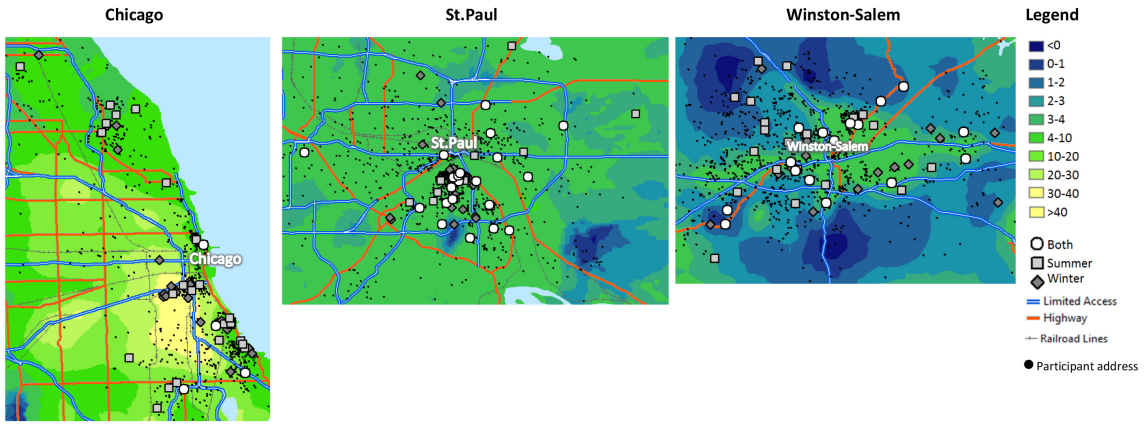

Silicon
R2 = 0.77
R2 = 0.93
R2 = 0.80
Predictions
Measurements
Zinc
R2= 0.80
R2 = 0.58
R2 = 0.58
Predictions
Measurements

Figure 2.


Chicago
St.Paul
Winston-Salem
Legend [a]
PM10-2.5
<2
2-2.5
2.5-3
3-3.5
3.5-4
4-6
6-8
8-10
>10
Both
Summer
Winter
Limited Access
Highway
Railroad Lines
Participant address [b]
Cu
<1
1-2
2-3
3-4
4-5
5-6
6-8
8-10
10-12
>12
Both
Summer
Winter
Limited Access
Highway
Railroad Lines
Participant address


Chicago
St.Paul
Winston-Salem
Legend
P
Si
<10
10-12
12-14
14-16
16-18
18-19
20-21
21-22
>22
Both
Summer
Winter
Limited Access
Highway
Railroad Lines
Participant address
<.3
.3-.325
.325-.35
.35-.375
.375-.4
.4-.45
.45-.475
.475-.5
.5-.6
>.6

Zn



[a] Bins were chosen to highlight within city contrasts and are not even.
[b] Participants' locations have been jittered.